Semi-Annual Report
July 1966

ADHESION BETWEEN ATOMICALLY PURE METALLIC SURFACES

PART IV

by

D. V. Keller, Jr.

Associate Professor of Metallurgy

Department of Chemical Engineering and Metallurgy

with

K. Johnson - Post-Doctoral Assistant

W. Saunders - Research Assistant

Prepared for

National Aeronautics and Space Administration

Office of Grants and Research Contracts, Code SC

Washington, D.C.

Grant No. NSG-483-1

SYRACUSE UNIVERSITY RESEARCH INSTITUTE

Department of Chemical Engineering and Metallurgy

Met. 1100-667SA

Semi-Annual Report
July 1966

ADHESION BETWEEN ATOMICALLY PURE METALLIC SURFACES

PART IV

by

D. V. Keller, Jr.

Associate Professor of Metallurgy

Department of Chemical Engineering and Metallurgy

with

K. Johnson - Post-Doctoral Assistant

W. Saunders - Research Assistant

Prepared for

National Aeronautics and Space Administration

Office of Grants and Research Contracts, Code SC

Washington, D.C.

Grant No. NSG-483-1

SYRACUSE UNIVERSITY RESEARCH INSTITUTE

Department of Chemical Engineering and Metallurgy

Met. 1100-667SA

SECTION I

THE INTERPRETATION OF METALLIC ADHESION DATA

I. THE INTERPRETATION OF METALLIC ADHESION DATA

The measurement of metal-metal adhesion under ultra-high vacuum conditions has received considerable attention in the past few years (1-4). The various devices and techniques which have been applied to the problem are most numerous while the validity of the output data is somewhat perplexing. For example, Table I indicates that the spread in the coefficient of adhesion (ratio of the load to break an adhesion junction to the load to make that junction) for copper-copper contacts varies from zero and, in turn, through the ranges of 0.01, 0.1, 1.0 and 10. Such a variation certainly does not aid a designer in choosing materials for compatibility in a friction assembly which is expected to operate under dry conditions in hard vacuum. And, such a variation in results also leads one to suspect all adhesion data and the very mechanisms which have been proposed to justify cold welding. Since the adhesion theory of friction strongly incorporates the phenomena of adhesion, there is little question as to why certain friction theorists challenge the adhesion approach (5).

Let us briefly re-examine the theoretical basis for adhesion between two metals in order to identify those mechanisms which will prevent or inhibit the process. As indicated previously (6), probably the best model for examining adhesion systems seems to be the reverse of the ideal cleavage experiment which will only apply to a metallic system if the plastic deformation process during the cleavage can be accounted. Gilman (7) has shown that this is acceptable for some metallic systems which have an easy cleavage plane, i.e. zinc. Through this relation, the adhesion energy must be closely allied to the cleavage energy of a metallic system; and thus, the junction formed in an ideal adhesion experiment ought to be nearly equal to the fracture energy of that material which, in turn, will account for the plastic deformation occurring in medium to high temperature tests.

TABLE I

ADHESION DATA FOR COPPER-COPPER

UNDER VARIOUS CONDITIONS

Temperature °C	Time of Contact	$\alpha = \frac{\text{Force to break}}{\text{Force to make}}$	Remarks	Reference
25°C	1 min.	0.0228 0.0126 0.0300 0.0513 0.0600	Pressure 8×10^{-9} - 10^{-8} Torr heavily loaded	Ham (1)
25°C	15	0.0 0.05 0.07 0.09 0.15 0.20	Pressure 6×10^{-9} Torr list in increasing load to 2500 lbs., surfaces cleaned 2 min. with argon ions.	Horton (2)
150°C 300 300 500 500 500	7×10^4 sec. 1×10^4 1×10^4 10 100 7×10^4	0.0 0.0 0.089 0.037 0.21 1.46	Pressure below 5×10^{-9} Torr loaded to 80% of load to permit creep	Winslow (3)
25°C	short time	0.40 3.8 4.2	Oxides present < 10^{-9} Torr surfaces thermally degassed surfaces heavily worked (sliding) (1000 gram loading all cases).	Buckley (4)

Since we are considering pure metal adhesion, such as copper-copper, at room temperature, one should, therefore, be able to relate the strength per unit area of the interface directly to the ultimate tensile strength of copper; the observed data (cf. Table I), however, suggests that this is not always true since under certain circumstances no adhesion is observed. Three mechanisms have been proposed to justify the lack of adhesion in a system in which adhesion should theoretically be observed:

a) the presence of an impurity, oxide, etc. (8),

b) the release of elastic stresses which were imposed on the system during the loading process (8),

c) the presence of an energy barrier in the interface which must be overcome before atomic bonds can form across the interface (9).

Since (b) and (c) are operative, if true, on atomically clean surfaces and (a) is a contaminant barrier having little to do with the metallic state, a series of experiments on very clean surfaces ought to verify the validity of the two latter cases and illustrate the significance of the former. Such a series of experiments were conducted in this laboratory as discussed in the January, 1966 progress report (10) and concluded that the only barrier to adhesion of couples made from silver-silver, copper-nickel and silver-nickel was surface contamination. The other proposed mechanisms, if present, contributed so little to the mechanism that they were unobserved.

The major feature involved in the series of tests was the incorporation of a parallel experiment which qualitatively reflected the nature of the adhesion interface under test-during that test: from initial contact, to peak load, to fracture of the adhesion junction. The parallel experiment was the measurement of the contact resistance of the junction

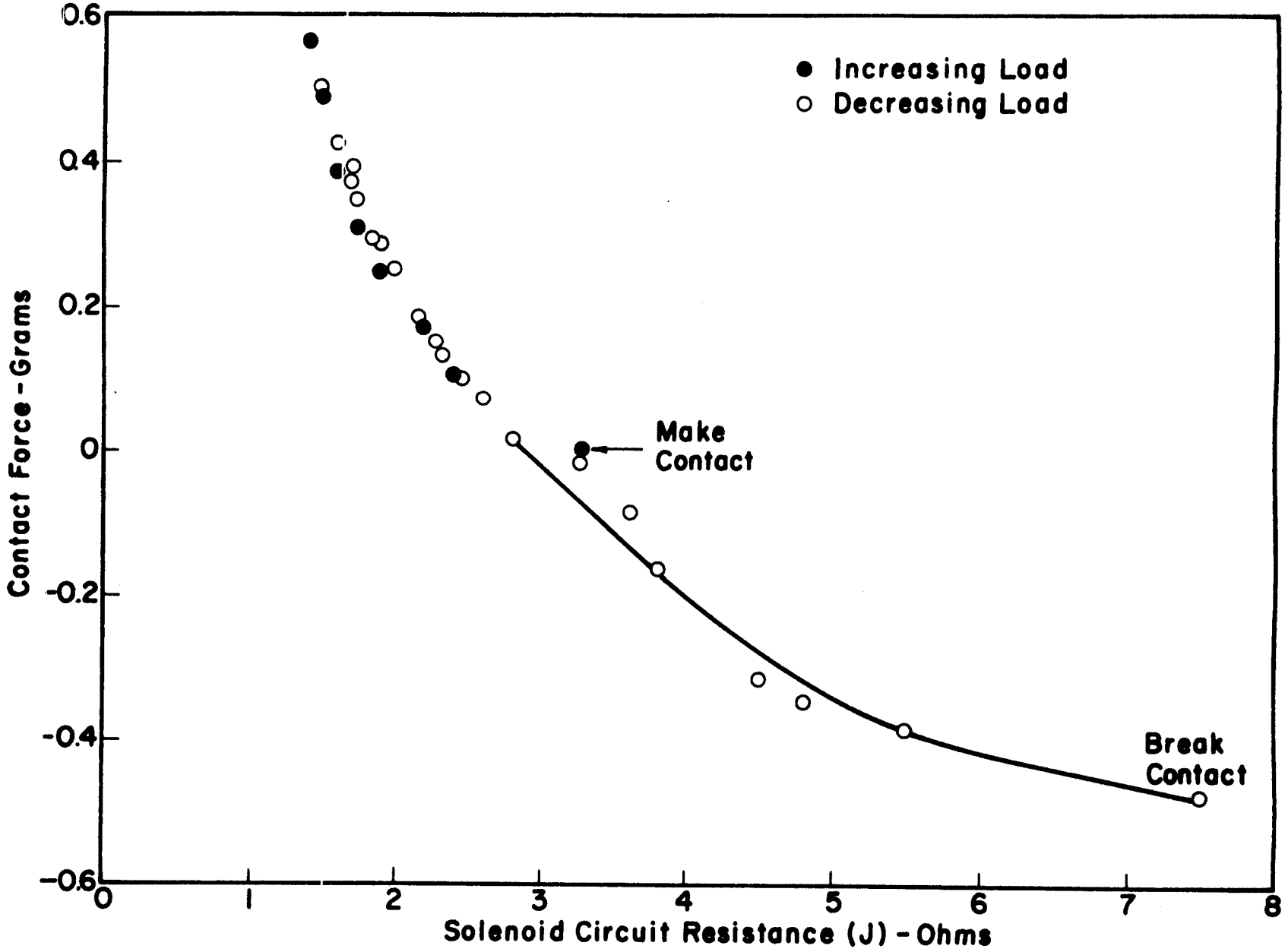
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
1
2
3
4
5
6
7
8
Contact Force - Grams
Solenoid Circuit Resistance (J) - Ohms
Increasing Load
Decreasing Load
Make Contact
Break Contact

Figure 1a

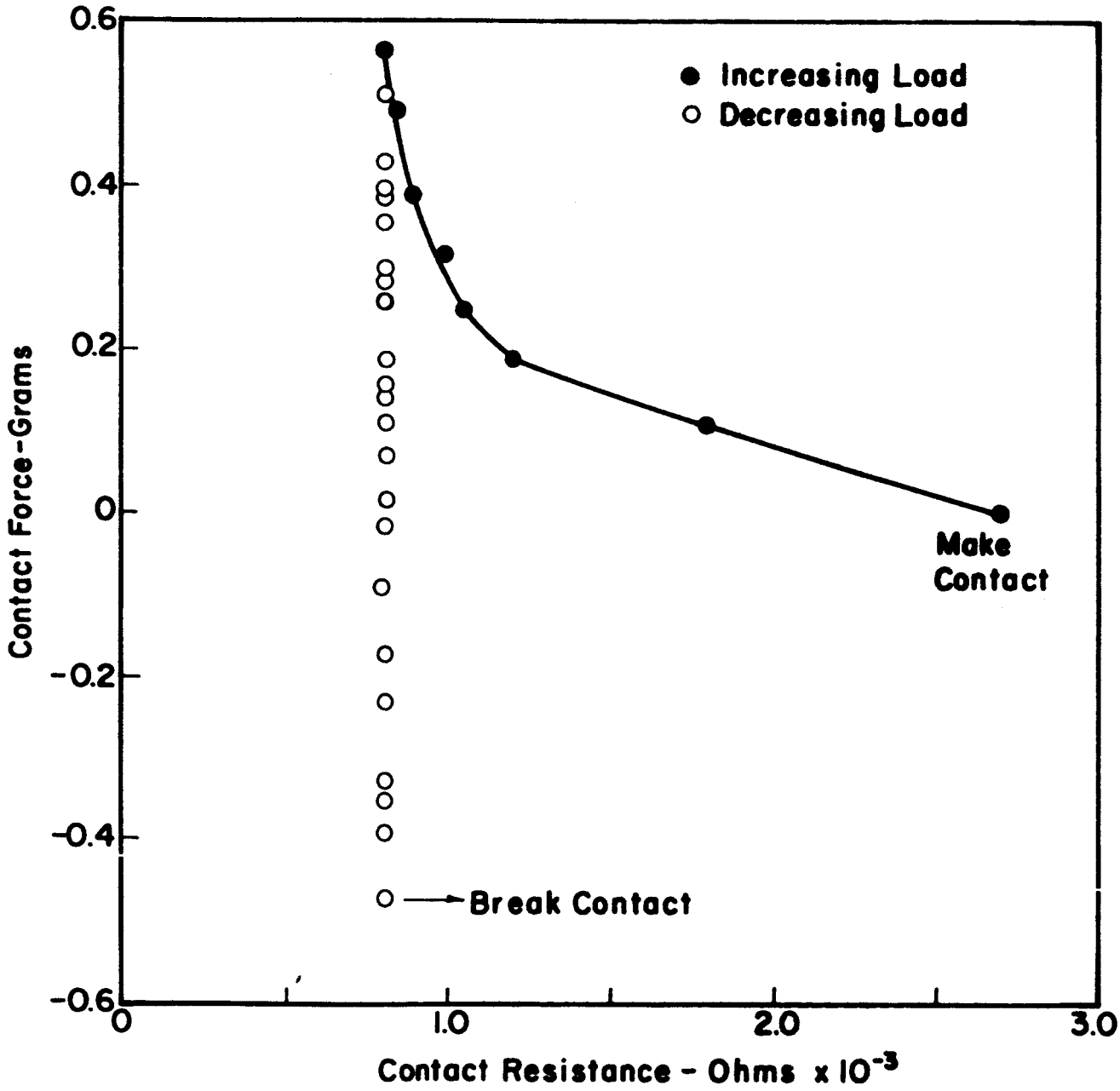
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
1.0
2.0
3.0
Contact Force-Grams
Contact Resistance - Ohms x 10^{-3}
Increasing Load
Decreasing Load
Make Contact
Break Contact

Figure 1b

under a very low impressed voltage such that contact heating could be considered nil (11). Under various contaminant conditions the junction resistance can vary from infinity (insulating oxide layer) through non-ohmic, or semiconductive, to pure ohmic as thoroughly discussed by Holm (12). Since the relationship of contact resistance to the contact area is not simple, the contact resistance data cannot be utilized in an absolute sense; however, the data are most valuable in a relative sense for comparing the degree of interference to electron flow through the contact region, e.g. contamination, from one stage of contamination to another as well as studying the effect of contact force on the change in contact area in one experiment. Let us examine the results of one adhesion cycle (contact, to maximum load, to fracture) under conditions in which the surfaces of silver-silver could be considered very nearly atomically clean (again the absolute sense is not justified since no internal measurement such as low energy electron diffraction techniques were employed to justify absolute cleanliness). The adhesion cycle illustrated in Figure 1a shows the effect of variation of the solenoid current (as circuit resistance), which tended to rotate the torsion balance arm in order to bring the silver samples into contact versus the contact force strain gauge reading. The moment of contact of the samples is observed as the first contact resistance value as shown in Figure 1b. The samples used to produce these curves were rigorously outgassed at 10^{-10} Torr and then subjected to rigorous argon ion cleaning at a current density of at least 500 amps/cm^2 at one kilovolt for about one hour in spectrographically pure argon. Since these curves are representative of the over five hundred tests to date of which a major portion of the curves did demonstrate adhesion, we feel that a curve of the shape shown in Figure 1b can be used as a criteria for adhesion. That is, as the load

is released the contact resistance is virtually constant until, or very close to, the point of fracture. This observation indicates that released elastic stresses do not play a major role in the fracture of silver-silver (Ag-Ni or Cu-Ni) adhesion junctions (recent tests show that this is also true in the titanium-titanium system where testing is all in the elastic range). In comparing an adhesion case to one in which contamination prevented adhesion in the silver-silver system, two factors were immediately evident in the lightly loaded systems under test. As shown in Figure 1c a substantial load of approximately 0.3 gms was required to permit a stable resistance reading, and after peak loading the released elastic stresses apparently decreased the contact area, such that the contact resistance superimposed along the loading curve returning to the point of instability. Whether or not this represents the ability of the contaminant oxides along the interface to fracture with ease or their total inability to form an adhesion junction cannot be readily ascertained from this experiment. What is important is that a distinction between weak and strong interaction can be made through a secondary measurement which provides some insight into the status of the interface. Note the difference in contact loading values versus contact resistance values between Figures 1b and 1c.

To explore this fact further Figure 2 shows the data from Figure 1b plotted as a log-log relationship with a curve for the variation in contact resistance of crossed silver wires tested in air. Of significance is the fact that for a constant load the removal of the contaminant layer from silver reduces the contact resistance by a factor of six, which is significant, since the precision with which this difference can be measured is about three or four significant figures without taking any special precautions. The variation of contact resistance with load as

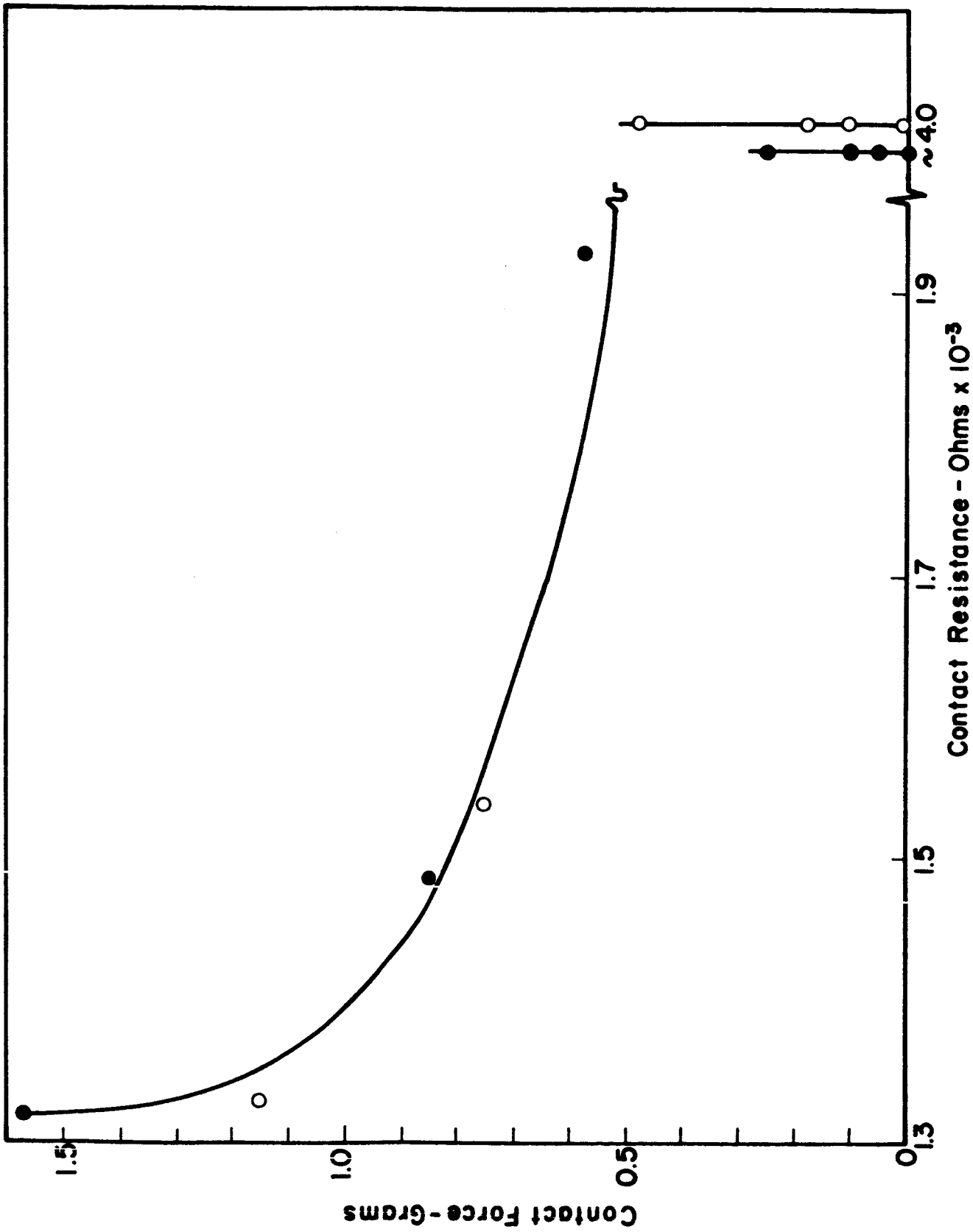
Contact Force - Grams
1.5
1.0
0.5
0
1.3
1.5
1.7
1.9
~4.0
Contact Resistance - Ohms x 10⁻³

Figure 1c

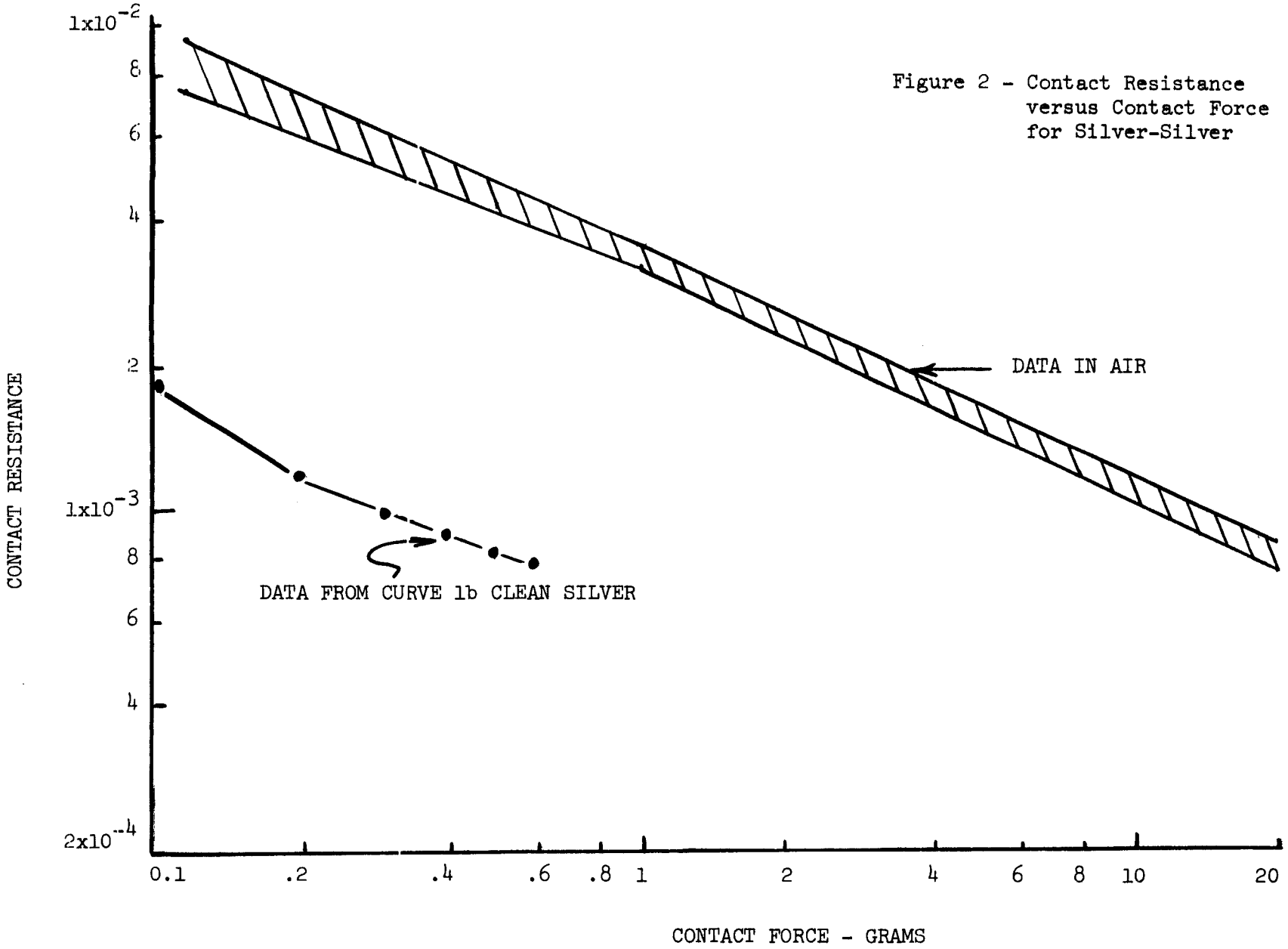

Figure 2 - Contact Resistance versus Contact Force for Silver-Silver

the cleaning process proceeds is also of interest, for it demonstrates changes that take place in the contact region as the ambient conditions change. Figure 3 shows the variation in contact resistance of the silver-silver system versus load beginning with etched silver samples in air, and comparing these values with those in vacuum, and, thereafter, with those in vacuum after bake-out (450°C - 20 hours) and 900°C anneal at 10^{-10} Torr, and finally after argon ion cleaning. No adhesion was indicated until after the preliminary degassing process was completed, and the junction strength only reached the strength of silver only after argon ion cleaning. The contaminant films present on silver seem to be of two distinct types, those which are partially removable by vacuum and degassing techniques and those which are only removable by rigorous ion cleaning techniques. The latter is supported by the observations of a very tenacious film on silver by Farnsworth and Winch (13) during their investigation of the work function of silver. Therefore, in a qualitative sense contact resistance measurements provide a simple method for the interpretation boundary conditions during adhesion testing. With a large quantity of data one is tempted to investigate just how far these observations can be interpretated; and in this line of thought, Figure 4 was developed. By expanding the coordinates of Figure 3 one can examine the data from very clean surfaces and adsorbed films in detail. Again, each point represents the minimum contact resistance observed in a particular adhesion cycle under various conditions of contamination. The curves have no real significance, but only act as a guide line to the surface conditions that might be expected by the particular experimental conditions. Whether or not the points in the ultra-clean region are truly the minimum values of contact resistance can only be ascertained by either a separate experiment (low energy electron diffraction) or a multitude of data from separate experiments on silver. Figures 5

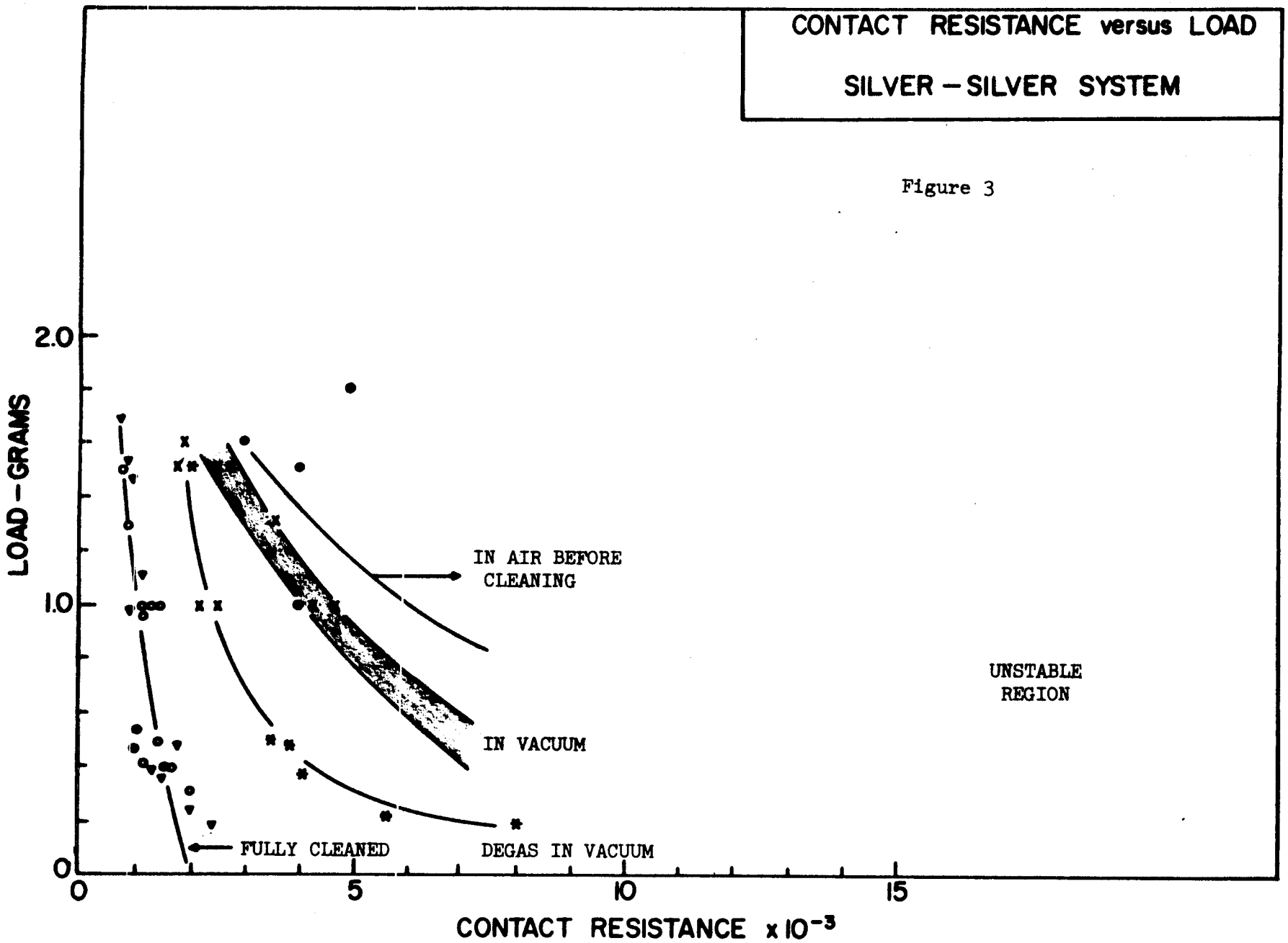
CONTACT RESISTANCE versus LOAD
SILVER – SILVER SYSTEM
LOAD – GRAMS
2.0
1.0
0
0
5
10
15
CONTACT RESISTANCE x 10⁻³
IN AIR BEFORE CLEANING
IN VACUUM
UNSTABLE REGION
FULLY CLEANED
DEGAS IN VACUUM

Figure 3

and 6 are similar to Figure 4 except that dissimilar couples were used. Again, the contact resistance reflects the nature of the film, but only in a qualitative fashion.

The necessity of maintaining a qualitative sense to the analysis with regards to the absolute contact resistance data discussed above can be justified briefly. The resistance (R) to current flow across a metal contact interface can be represented by

$$R = R_o + R_M$$

where R_o represents the resistance due to an oxide, or contaminant film, which, if thick enough, can be the controlling factor, i.e. act as a pure insulator. R_M is the constriction, or contact resistance due to the compression of the potential lines of force in a metallic contact from one macro-body through a very small diameter contact back to a second macro-body. The variation of R_o with surface cleaning ought to be from infinity, or pure insulator, through semi-conducting for extremely thin films to zero for atomically clean surfaces. The variation, however, is probably affected by the contact pressure as well as the area change during load variation, and is probably a most complex function of load and contaminant chemistry. The theoretical nature of R_M was developed by Holm (12) and has recently been re-analyzed by Greenwood (14), who showed that R_M is a function of the metal conductivity (ρ) and the number (n) of metal junctions by the equation,

$$R_M = \rho \left(\frac{1}{\pi n^2} \sum_{i \neq j} \sum \frac{1}{r_{ij}} + \frac{1}{2 \sum_i a_i}\right)$$

where r_{ij} = is the distance between n metal contacts

a_i = radius of the ith contact

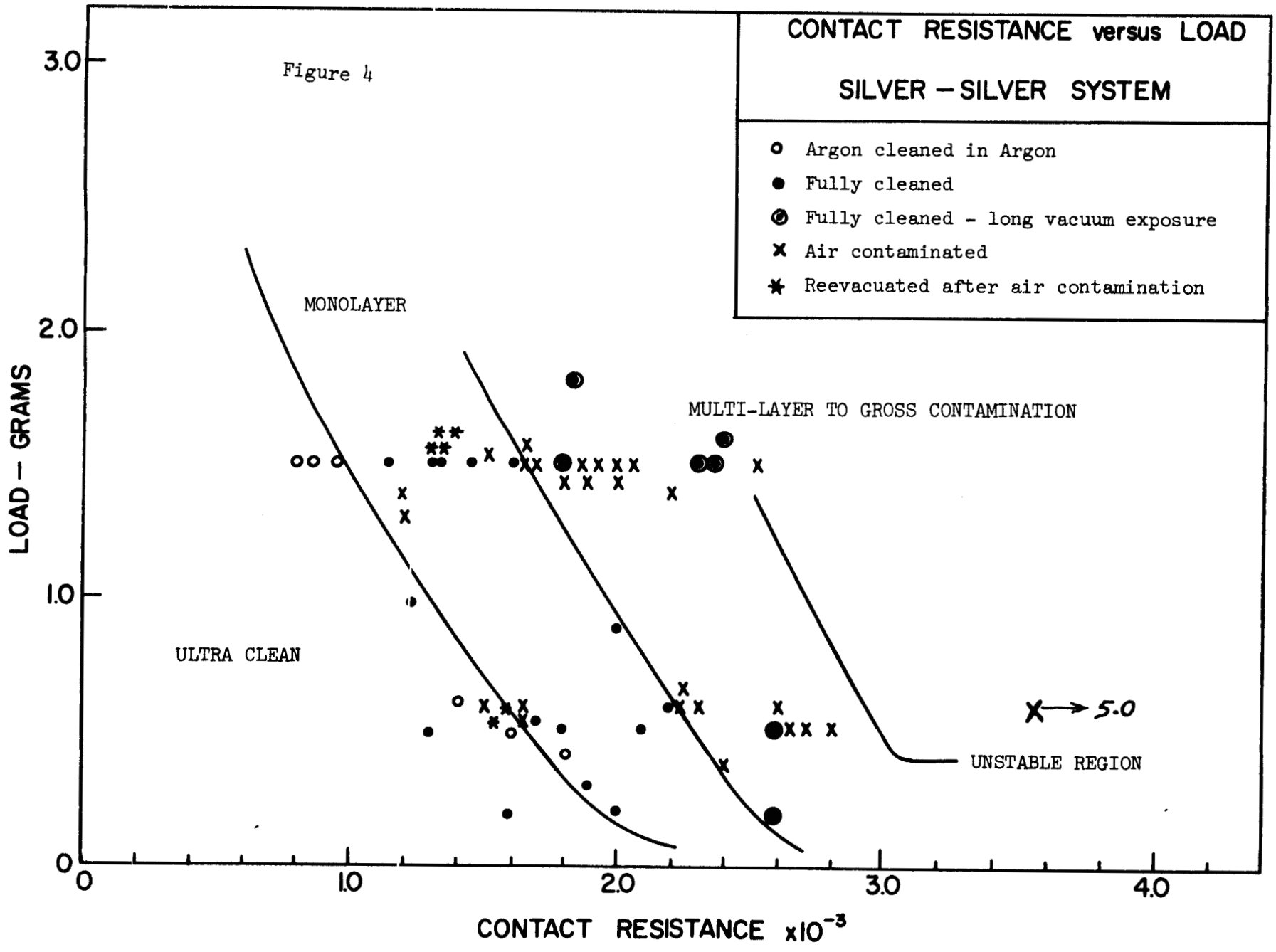
Figure 4
CONTACT RESISTANCE versus LOAD
SILVER – SILVER SYSTEM
Argon cleaned in Argon
Fully cleaned
Fully cleaned - long vacuum exposure
Air contaminated
Reevacuated after air contamination
MONOLAYER
MULTI-LAYER TO GROSS CONTAMINATION
ULTRA CLEAN
UNSTABLE REGION
5.0
LOAD – GRAMS
CONTACT RESISTANCE x10⁻³
0
1.0
2.0
3.0
4.0

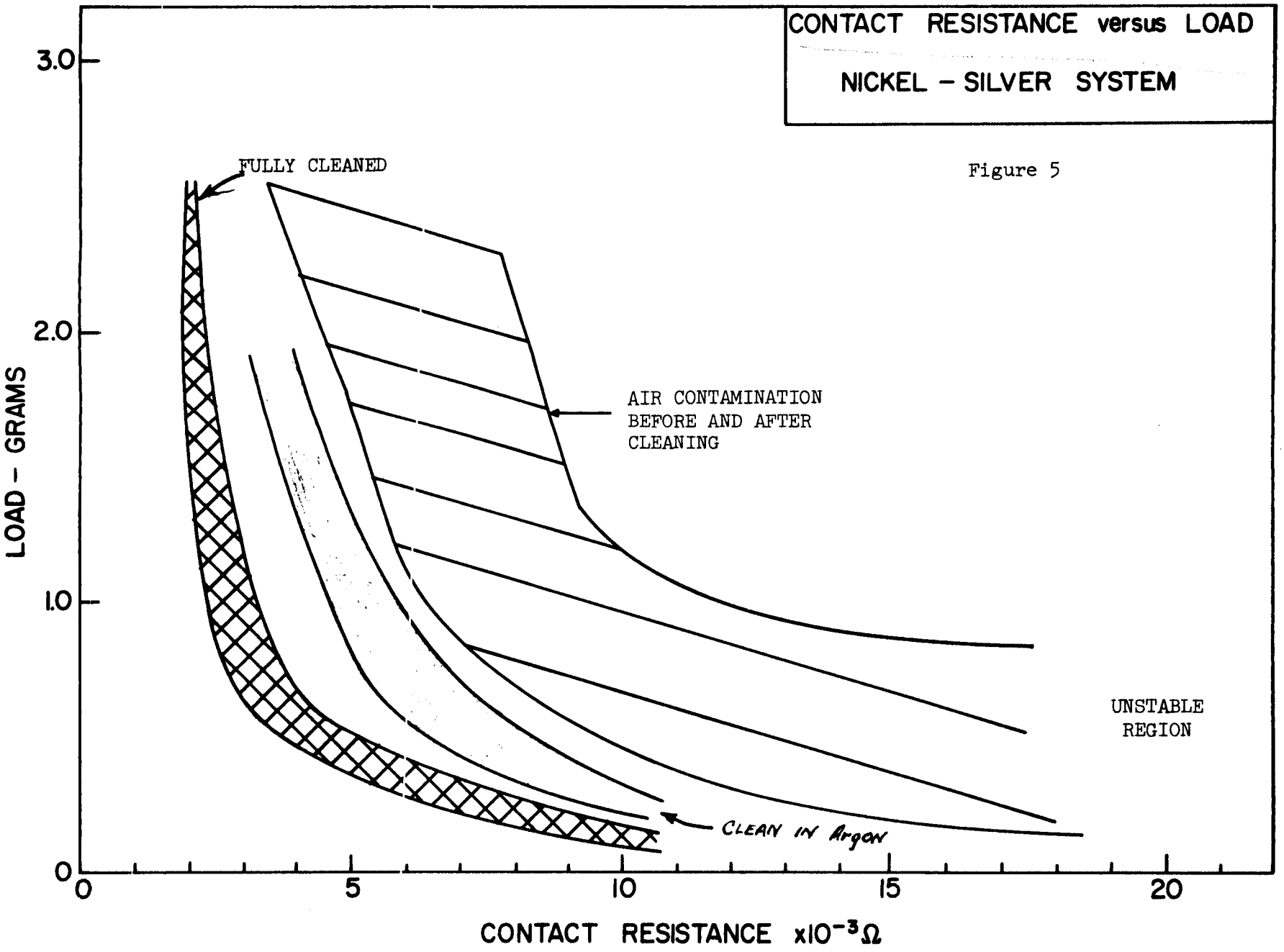
CONTACT RESISTANCE versus LOAD
NICKEL - SILVER SYSTEM
FULLY CLEANED
AIR CONTAMINATION
BEFORE AND AFTER
CLEANING
UNSTABLE
REGION
CLEAN IN Argon
LOAD - GRAMS
CONTACT RESISTANCE x10⁻³Ω
3.0
2.0
1.0
0
0
5
10
15
20

Figure 5

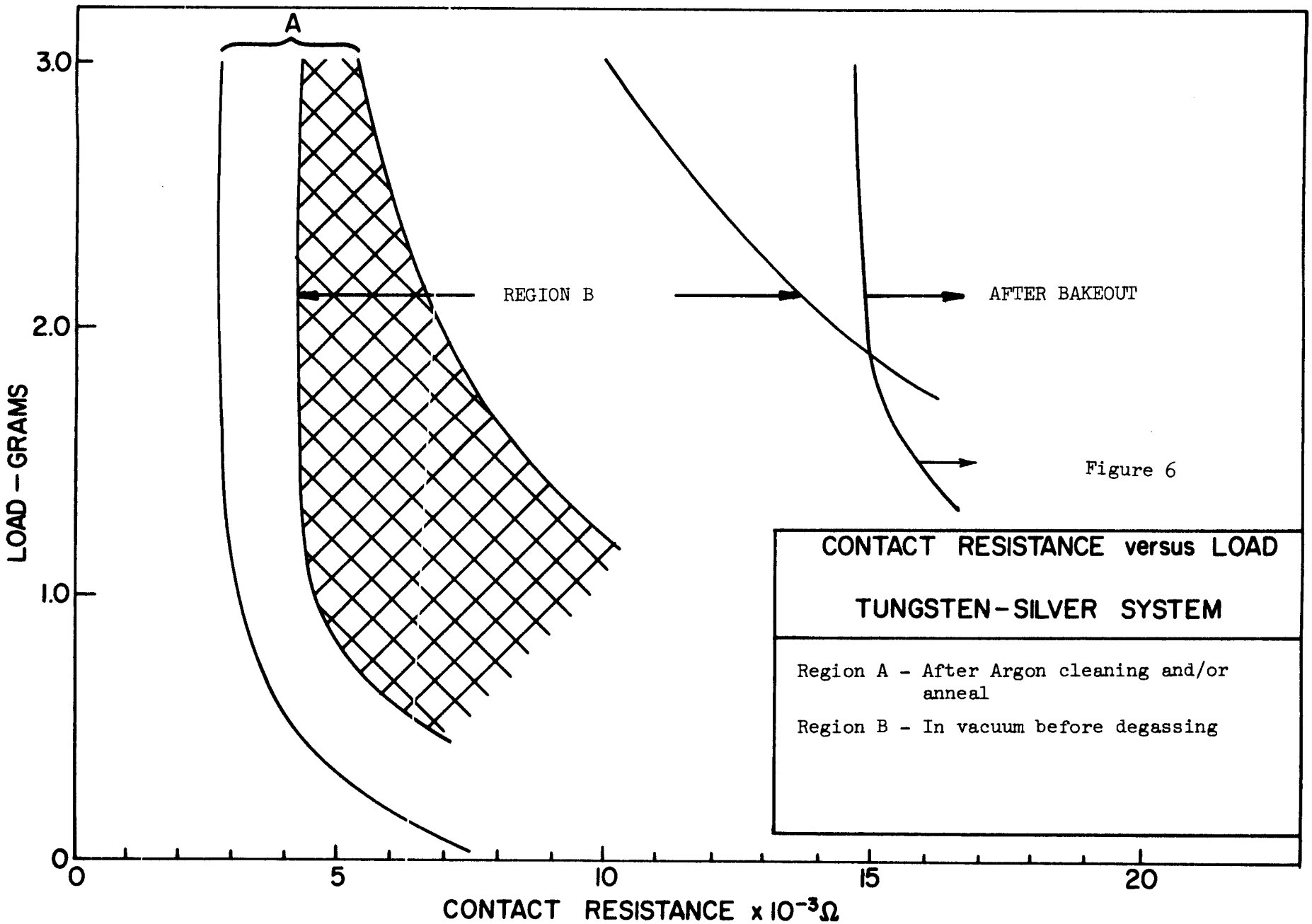

Figure 6

CONTACT RESISTANCE versus LOAD

TUNGSTEN–SILVER SYSTEM

Region A – After Argon cleaning and/or anneal

Region B – In vacuum before degassing

Since a metal contact region may have any number of asperities of various diameters in real contact at any variation in separation, the equation, in effect, indicates there is little hope for reasonable analysis from basic principles. Whether or not an empirical relationship can be established based on a simple model (10) remains to be seen. The linearity of the data shown in Figure 1b when it was plotted on a log-log curve (Figure 3) indicates Holm's single contact relationship for clean surfaces,

$$R_M = \frac{\rho}{2a}$$

where a = the contact radius which, in turn, is a function of the deformation properties of the material versus load

is a reasonable approximation and some hope that an empirical relations may evolve. Further evidence of this was established when the log of the contact resistance versus the log of the load of the individual adhesion cycles were plotted and, for the most part, produced straight lines with a slope lying between $(-\frac{1}{3})$ or $(-\frac{1}{2})$. The minus one third slope represents an area variation due to elastic deformation of the metal and the latter due to plastic deformation (12). The intercepts of these lines were also of the right order of magnitude, but displaced between 10-40%, which was probably due to contamination or multi contact points and did not seem too far removed, considering the complexity of the proposed mathematical relationships.

Exactly where does this place the contact resistance type of experiment in the realm of adhesion testing? Firstly, let us examine the coefficient of adhesion parameter obtained from the silver-silver experiments with the realization that this parameter assumes that the elastic and plastic deformation in forming the contact junction was equal to that during the fracture of that junction. Of course, one bears no relationship to the other, so the numbers are not wholly

significant, but if accepted in a relative sense, they do offer a comparison. Table II illustrates the extreme effect of the atmosphere on the relative strength of the adhesion junction. The air cited in the table was dried over silica gel for several days prior to use; however, in exploiting this behavior further, individual pure gases, i.e. nitrogen, oxygen, hydrogen and water, are in the process of being examined to ascertain which has the greater effect as a barrier in the adhesion process. The use of various chemical agents was also proposed in an attempt to optimize the process. As the various atmospheres are examined the contact resistance data is also accumulated during the test, which will: a) permit a qualitative picture of the fracture process, e.g. Figure 1b; b) some indication of the relative thickness of the film by contact resistance value; and, c) hopefully, a reasonable correlation of the resistance values with area will be achieved which, in turn, will provide an accurate knowledge of the real contact area. If a knowledge of the real contact area can be obtained, the testing data can then be reduced to an absolute scale and related to the mechanical properties of the material in test.

The development of the adhesion contact resistance experiment, if nothing else, permits three independent simultaneous indications of the presence or absence of adhesion, and permits two independent measures of the strength of the junction formed. On this basis, we feel that the reliability of metallic adhesion data will be increased; and, as a side effect, some insight into the behavior of contaminant films will be gained. Furthermore, as the confidence level of adhesion data is expanded two very fruitful areas of investigation are immediately available, namely, the effect of alloy constituents on metallic adhesion and the effect of specific chemical agents, either in metal solution or as gaseous contaminants on metallic adhesion can be investigated in a rather quantitative

TABLE II

APPROXIMATE COEFFICIENTS
FOR
ADHESION*

Pressure Torr	Conditions	Average α (at least 10 runs)
1. 10^{-10}	before cleaning	0 ≠
2. $\sim$ 4 mm argon	immediately after cleaning	2.2 ± 1.2
3. 8×10^{-9}	air inleak from 10^{-10} Torr after cleaning	0.33 ± 0.16
4. $\sim 10^{-4}$	air inleak from #3	0.19 ± 0.17
5. 760	air inleak from #4 10^{-10} Torr	0 ≠
6. 5×10^{-7}	after atmosphere exposure(s)	0.16 ± 0.08

*cross wire loading 0.01 - 2.0 grams at 25°C

≠minimum detectable α = 0.005

manner. Considerable data is already available on the effect of certain agents on the fracture strength of metal systems; e.g. the investigation of the embrittlement of metals with mercury, or by gallium, etc. by Rostocker (15) and Westwood (16), to cite a few. As a further example, the use of iodine as a specific agent to reduce the fracture strength in metal systems, as has been discussed recently by Owens, Roberts and Barnes (17), might be cited among the very many that are available. Since the above experimental discussion has related the adhesion strength to the fracture strength the utilization of surface chemistry as a basis for research direction in adhesion studies, would seem the most fruitful, particularly, if specific release agents, i.e. low shear stress boundary agents, were desired to reduce the adhesion component in friction systems.

BIBLIOGRAPHY

1. Ham, J.L., "Investigation of Adhesion and Cohesion of Metals in Ultra-High Vacuum", Final Report, 1963-NASA Contract NASw-734.

2. Horton, M.J., and Giammanco, R.P., "A Study of the Adhesion and Cohesion of Metals", Quart. Progress Report, June 1965, for NASA Contract NASw-468.

3. Winslow, P.M., and McIntyre, D.V., "Adhesion of Metals in Space Environment", J. Vac. Sci. and Tech., 3, 54 (1966).

4. Buckley, D.H., and Johnson, R.L., "Friction, Wear and Adhesion Characteristics of Titanium-Aluminum Alloys in Vacuum", NASA Tech. Note: TB-D-3235.

5. Rabinowicz, E., "Friction and Wear of Materials", J. Wiley and Sons, New York (1965).

6. Keller, D.V., Wear, 6, 353-365 (1963).

7. Gilman, J.J., J. Appl. Phys., 31, 2208 (1960).

8. Bowden, F.P., and Tabor, D., "The Friction and Lubrication of Solids, Part II", Clarendon Press, Oxford, England (1964).

9. Erdmann-Jesnitzer, F., Aluminum, 33, 730 (1957).

10. Keller, D.V., "Adhesion Between Atomically Pure Metallic Surfaces, Part IV", Semi-Annual Report, January 1966 for NASA-Grant NSG-483-1.

11. Williamson, J.B.P., Proc. Inst. Elect. Eng., 109A, #3, 224 (1962).

12. Holm, R., "Electric Contacts Handbook", Springer-Verlag, Berlin, Germany (1958).

13. Farnsworth, H.E., and Winch, R.P., Phys. Rev., 58, 812 (1940).

14. Greenwood, J.A., "Constriction Resistance and the Real Area of Contact", Burndy Research Division Report No. 38, Burndy Corporation, Norwalk, Conn., May 1966.

15. Rostoker, W., McCaughey, J.M., and Markus, H., "Embrittlement by Liquid Metals", Reinhold Pub., New York (1960).

16. Westwood, A.R.C., and Kamdar, W.M., Phil. Mag. 8, 787 (1963).

17. Owens, R.S., Roberts, R.W., and Barnes, W.J., Wear, 9, 79 (1966).

SECTION II

ADHESION OF HARD METALS IN ULTRA-HIGH VACUUM

Keith I. Johnson

I. INTRODUCTION

The factors affecting the adhesion of metals have long been in dispute. Earlier experiments have shown that there is a deformation barrier to adhesion which has to be surpassed before bonding between metal couples can occur, and that this barrier varies with the amount of contamination present, the hardness of the metal couples, their atomic crystal structure and the temperature of the experiment (1) (2). However, it was not possible, until recently, to control contamination in anymore than a gross sense. Consequently, the separation of the above variables has been virtually impossible. The advent of ultra-high vacuum techniques and the preliminary studies done on surface cleaning techniques by the low energy electron diffraction workers, however, has enabled attainment and maintenance of virtually atomically clean metal surfaces. The present work, therefore, was initiated in an attempt to study the adhesion characteristics of a wide range of such clean metal surfaces and the effect of their subsequent contamination.

Earlier adhesion studies on the silver-silver, silver-nickel (insoluble) and copper nickel (soluble) metal couples (3) ($\sim$ 0.40" dia. specimens), have shown that spontaneous adhesion occurred for these three systems at loads less than 0.1 grams, after the surfaces were cleaned by argon ion bombardment and maintained under a vacuum. Under these lightly loaded conditions, there is a substantial amount of elastic deformation and, consequently, the following conclusions may be drawn:

1. The major barrier to metallic adhesion, which is always encountered during the cold pressure welding of metals, is due to contamination from the surrounding atmosphere. This may be deduced since adhesion occurs between clean couples under such highly loaded conditions.

2. The postulated energy barrier to adhesion due to the necessity of realigning the surface atoms to form an interface is of minor or no importance for the couples studied, since adhesion occurred under such lightly loaded conditions.

3. No evidence for the rupture of bonds by the relief of elastic stresses during the unloading of the specimens was found for the softer metal couples of this study, although a substantial amount of elastic deformation was present. Such a bond rupture mechanism has been previously postulated (6) to explain the normally observed lack of adhesion under conditions where there is a substantial amount of elastic deformation.

4. The bulk miscibility criterion for the metallic adhesion of dissimilar metal couples does not apply to the insoluble silver-nickel couple studied, since adhesion occurred to the same degree as for the soluble Cu-Ni and the Ag-Ag couples. It had been previously stated that insoluble metal couples would not adhere (7).

The present report deals with the attempt to extend the above study to harder metals. It is well known that harder metals are more difficult to cold weld than soft, but the reason for this is not clear. Thus, contamination may be more of a barrier for these materials, or the above postulated energy barrier, and the role of elastic relief stresses on unloading may be more important here than in the above softer metal couples. Thus, adhesion studies on the W-W and Mo-Mo systems have been initiated. The Ti-Ti system has also been studied since its hardness is intermediate between those of the above harder and softer metal couples, and also because titanium has a close packed hexagonal atomic structure at room temperature. Hexagonal metals have previously been reported to

adhere to a lesser degree than metals with a cubic structure (1) (2). These former studies, however, were done in the presence of gross contamination and, consequently, the present examination has been initiated in an effort to determine whether the hexagonal metals are inherently more difficult to cold weld, or whether the effect is due to contamination.

II. EXPERIMENTAL PROCEDURE

The adhesion cell and pumping system were designed to allow for the measurement of the contact resistance and adhesion between two metal samples as a function of contact force, with varying degrees of surface contamination. The system used consisted of a 40 x 300 mm pyrex adhesion cell (A) attached to a 1" ultra-high vacuum valve (H) and thence to the vacuum system, as shown in Figure 1. The adhesion cell, valve, and first liquid nitrogen trap were baked out during each experiment at 450°C for at least 10 hours. After bakeout, the degassing of the titanium sorption pump, and the cooling of the first liquid nitrogen trap, the minimum pressure observed in the adhesion cell was 5×10^{-10} Torr, as measured by the NRC Redhead gauge (D) mounted adjacent to the specimens. The titanium sorption pump (E) consisted of a helix of 0.010" titanium wire closely wrapped over 0.015" tungsten wire.

The torsion beam and adhesion samples are shown in Figure 2. Both were supported by three 5 mm stainless steel support rods heliarc welded to a stainless steel Conflat flange plate attached to the cell at (J), Figure 1. The rods also served as supports for the sample electrical leads within the chamber, which were all insulated with recrystallized alumina tubing and left the cell by standard Kovar through-seals at (B), Figure 1. The torsion beam was also constructed of alumina tubing and was supported at its center by a stainless steel connector which served as a bearing for the torsion beam as it rested on a 0.010" tungsten wire under tension between the two 5 mm stainless steel supports.

The iron slug, F_1, Figure 2, fixed to the end of the torsion beam, was used in conjunction with the external permanent magnet (C), to affix the position of the indenter with respect to the sample plate. The strain

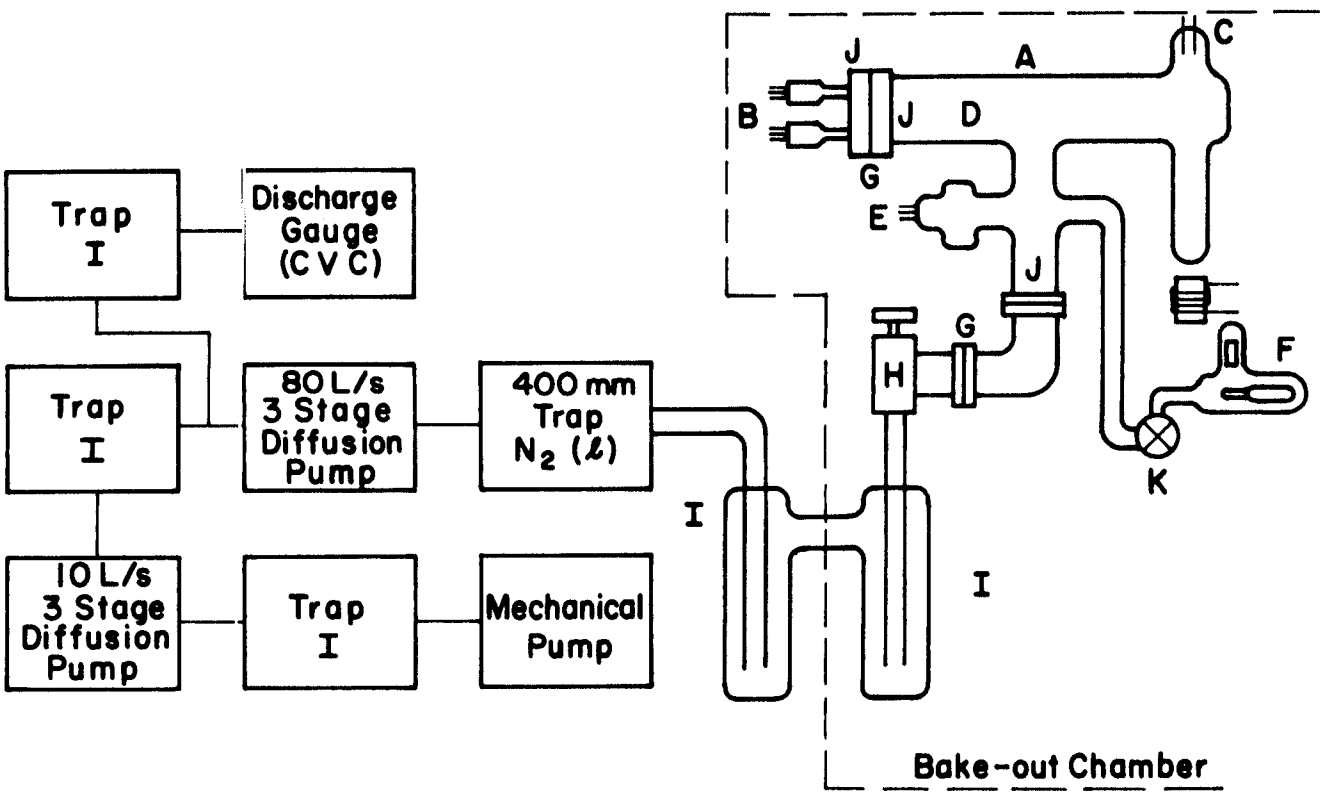

Figure 1 - Diagrammatic sketch of vacuum system where, A is the adhesion cell, B the electrical leads into the cell, C the strain gauge leads, D the Redhead gauge, E the titanium sorption pump, F the argon source, G the conflat flanges, H the 1" Granville-Phillips valve, I the 300 mm liquid nitrogen traps, J the Pyrex-Kovar seals, and K the 1/2" Granville-Phillips valve.

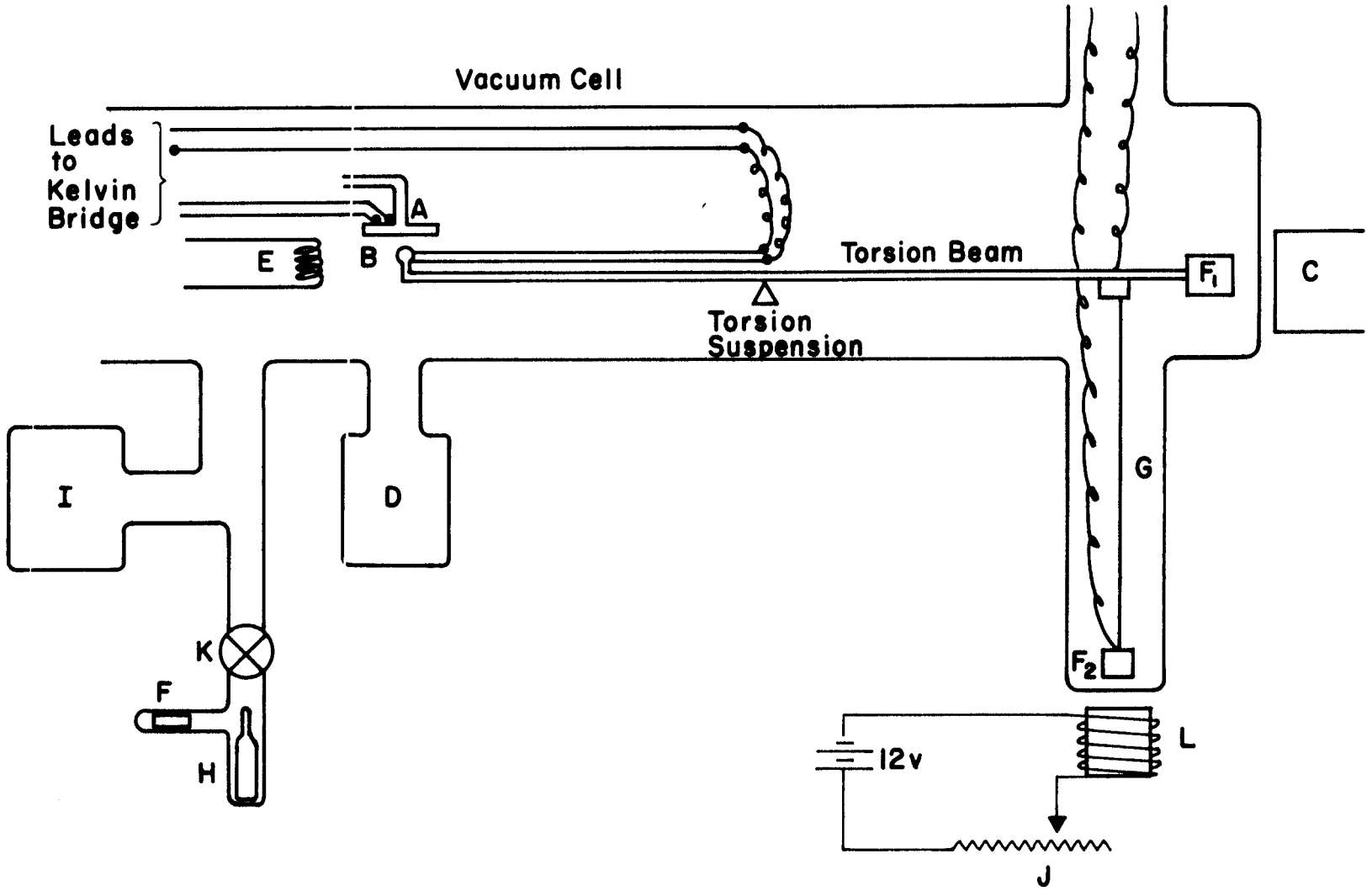

Figure 2 - Diagrammatic sketch of adhesion cell where, A is the sample plate, B the sample indenter, C the positioning magnet, D the Redhead gauge, E a filament, F the iron slugs, G the strain gauge assembly, H the argon capsule, I the titanium sorption pump, J the calibrated variable resistance, K the 1/2" Granville-Phillips valve, and L the load solenoid.

gauge (G) mounted on the torsion beam, supported a second iron slug, F_2, which interacted with the field of a solenoid (L). Thus, as the current in the solenoid, monitored by the calibrated variable resistance (J) was increased, the torsion beam was moved into sample contact and a normal force placed on the sample plate due to the indenter. The force of shearing the magnetic flux between the iron slug, F_1, and the magnet (C) before contact, and the force of contact of the indenter (B) with the fixed sample plate (A) were measured by the 0.00095" x 6" nude straight constantan wire strain gauge, whose output was monitored by a Sanborn Transducer-Amplifier, Model 312. Prior to each experiment the balance system was calibrated in air throughout the range of operation, i.e. 0 - 2.0 grams, and was found to have a sensitivity of about ± 0.010 grams.

The contact resistance between the indenter and plate was measured with a Precision Kelvin Bridge in conjunction with a Nanovoltmeter used as a null detector. A source was used such that the potential drop across the contact resistance was approximately 0.3 millivolts, which should yield negligible temperature rise at the contact region due to current flow (8). Such an arrangement enabled the resistance to be measured when within the range of zero to one ohm, with an accuracy of 3-4 figures. The resistance circuit was calibrated with a 0.01 ohm NBS standard resistor prior to each run.

The torsion beam arrangement was designed in the above way in order to obtain, as nearly as possible, pure normal loading. Thus, shear deformation of the adhesion specimens was reduced to a minimum during test cycles, the only tangential motion being imparted to the specimens by unavoidable normal laboratory vibrations. The effects of these could only be observed under extreme light specimen loading and non-adhesion conditions,

when instability of the contact resistance occurred.

The normal operating procedure involved placing the samples in the system and evacuating to a pressure below 10^{-5} Torr, at which time the bakeout cycle was imposed, as previously mentioned, to attain an ultimate pressure of about 5×10^{-10} Torr. At this time the ultra-high purity argon, obtained from Airco Company, was admitted to the leak system by breaking the capsule break-off tip. The argon was then admitted to the cell to a pressure of about 10^{-4} Torr, and argon ion bombardment of each surface initiated by placing a D.C. potential of about a kilovolt between the filament (E), Figure 2, and the surface to be cleaned. During the cleaning operation, which amounted to a total of at least three hours for each surface, a small nickel shield was moved into place (via magnet) to completely shield the surface not being cleaned from contamination by sputtered material. After bombardment, a substantial sputtered deposit on the cell walls attested to the fact that a considerable amount of surface material was removed from each sample. Upon completion of the argon ion bombardment phase, the system was evacuated and sample annealing initiated. Electron bombardment from the filament (E) was used to heat the sample for argon degassing and sample anneal.

At certain points throughout the whole of this evacuation and surface cleaning process a series of adhesion cycles were performed at room temperatures by slowly bringing indenter (B) into contact with (A), by reducing the variable resistance (J). The values of (J) and the deflection of the transducer amplifier, due to the strain gauge, were noted concurrently at discrete intervals until sample contact was made, when contact resistance measurements were also performed at each new adjustment of (J). The load on the adhesion couple was then further increased to a

predetermined level and then reduced by increments until contact was broken. Contact make and break were immediately indicated by a closed and open circuit in the Kelvin Bridge. In this way the loading and unloading processes were monitored by at least ten concurrent contact resistance, force, and solenoid circuit resistance measurements during each adhesion cycle. The peak loads employed were usually 0.3 and 1.5 grams.

In the present study the W-W, Ti-Ti and Mo-Mo systems were studied, .030" diameter cross wire specimens at A and B, Figure 2, being employed in all cases. The materials used were polycrystalline and of the highest purity normally available, i.e. W, 99.95%, Ti, 99.9%, and Mo, 99.95%, the suppliers being United Mineral and Chemical Corp., New York. The wires were mounted in the adhesion cell in the as-received condition.

III. RESULTS AND DISCUSSION

During the period covered by this report, a total of 30 adhesion cycles have been done under varying conditions on the W-W, 100 on the Ti-Ti, and 70 on the Mo-Mo couples. Only the Ti-Ti system has shown, as yet, any significant adhesion, although a tendency to adhesion has been shown by the Mo-Mo couple after a prolonged degas treatment.

Ti-Ti Results

No adhesion was observed in this couple except after argon ion bombardment of the surfaces, and generally only then after a prolonged degas treatment. Figure 3 shows a typical adhesion cycle done under these conditions. The load required to break the bond, 0.8 grams, is significant of adhesion, as is the maintenance and stability of the minimum resistance up to the bond break away point on unloading.

As mentioned above, the couple loading, and, consequently, the load to break any couple bond, may be measured quite accurately by the strain gauge attached to the adhesion beam. In order to make some estimation of the bond strengths, however, the contact area formed under maximum couple loading must be known. This is necessarily difficult due to the non-ideal geometry of the surfaces and also because the deformation is partially elastic and partially plastic in nature.

If the interaction between the crossed titanium wires is assumed to be totally elastic, the Hertzion equation (9),

$$a = \left[\frac{3}{4} P \left(\frac{1-\sigma_1^2}{E_1} + \frac{1-\sigma_2^2}{E_2} \right) \left(\frac{1}{r_1} + \frac{1}{r_2} \right)^{-1} \right]^{1/3} \qquad (1)$$

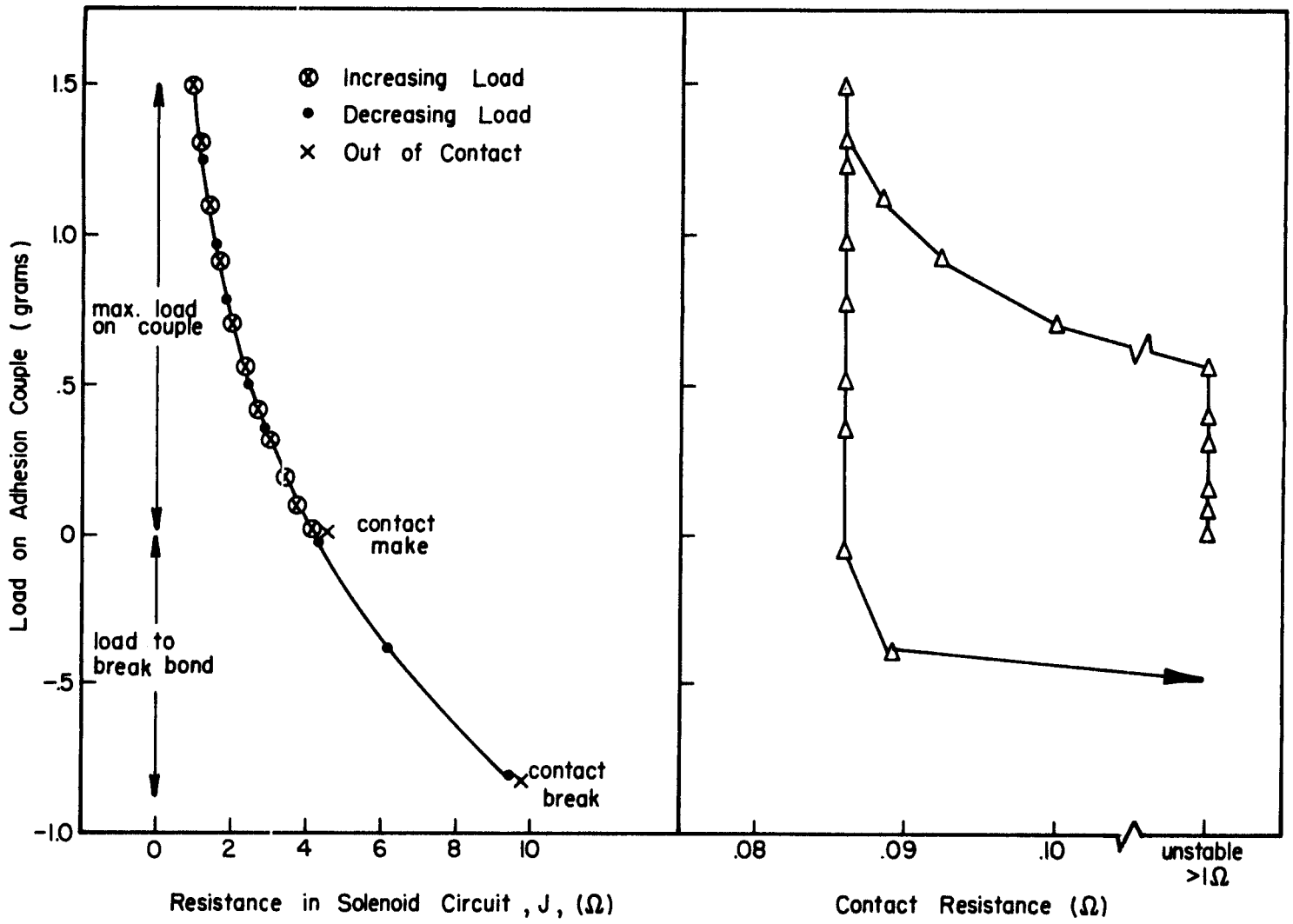

FIGURE 3 - Titanium-titanium adhesion cycle after second argon-ion bombardment (with intermediate electron bombardment degas, 1 hr. at ∿ 900°C), pressure - few microns of argon.

where

a = radius of the contact zone

r = radius of curvature of the wires

σ = Poisson's Ratio

E = Young's Modulus Elasticity

P = load on couple

enables an approximation of the contact area.

Such a simplified elastic interaction is justified in the case of the Ti-Ti couple, and even more so the cases of the harger W-W and Mo-Mo couples, since bulk plastic deformation does not occur on loading the couples until (10),

$$P_m = 1.1\ Y \qquad (2)$$

where

P_m = Pressure under indentor

and

Y = Yield strength of the material

This point is not reached in the titanium couple until the couple is subjected to a 1.7 gram loading.

Figure 4 shows a plot of the Ti-Ti joint strengths measured under various surface conditions, after loading the couple to about 0.3 and about 1.5 grams. The above elastic approximation was used to determine the contact areas. As may be seen there is no appreciable adhesion before surface cleaning. Only one series shows significant bond strengths after the first argon-ion bombardment treatment, but adhesion becomes more significant after specimen degas ($\sim$ 1 hr. at $>$ 900°C) and further argon ion bombardment. Bond strengths are, however, consistently below the bulk tensile strength of titanium. No bond strengths were generally observed for couple loadings of less than 0.3 grams.

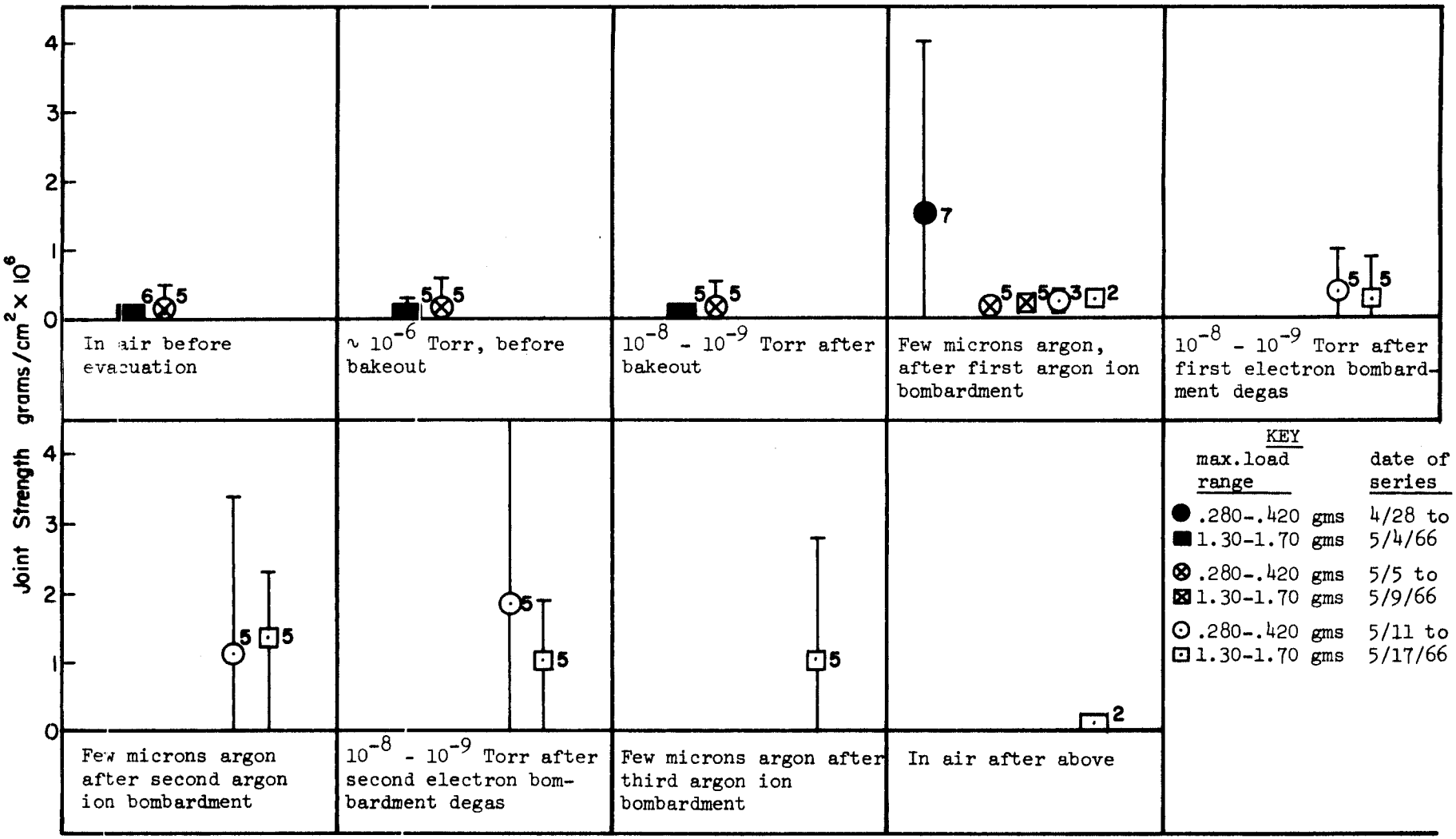

FIGURE 4 - Bond strengths of titanium-titanium couple under varying surface conditions, calculated using elastic contact area approximation. Figures beside averages denote the number of cycles measured. Tensile strength annealed bulk titanium = 55 x 10^6 gms/cm^2.

Mo-Mo Results

No significant adhesive force has yet been measured for the Mo-Mo couple, even after prolonged specimen degas ($\sim$ 30 hrs. at > 1,000°C) and argon ion bombardment cleaning procedures. After such rigorous cleaning, however, a tendency to maintain the minimum contact resistance on unloading the couple was observed, see Figure 5. This maintenance of contact resistance is an indication of adhesion, as has been substantiated in earlier work (3).

Because of a low energy electron diffraction study by Haas and Jackson (11) it was thought that carbon contamination could be responsible for this lack of adhesion. Consequently, one attempt has been made to remove any carbon present by heating the degassed Mo wires in an atmosphere of 10^{-6} Torr of ultra-pure oxygen. Due to a faulty oxygen supply, however, this experiment was not conclusive and no adhesion was observable.

W-W Results

No indications of adhesion have yet been observed for this system. In all tungsten experiments an initial high temperature degas was employed (> 2,000°C), since this has been claimed to give clean surfaces where insoluble impurities are present (12). On the subsequent opening of the adhesion cell, however, the tungsten wires were found to be severely embrittled. Such embrittlement of tungsten after annealing is a commonly observed phenomenon and is generally attributed to grain boundary contamination (13). Consequently, the tungsten surfaces of these studies were undoubtedly contaminated.

Interpretation of Data

Although significant adhesion has been observed in the titanium system and a tendency to adhesion was noted for the molybdenum couples

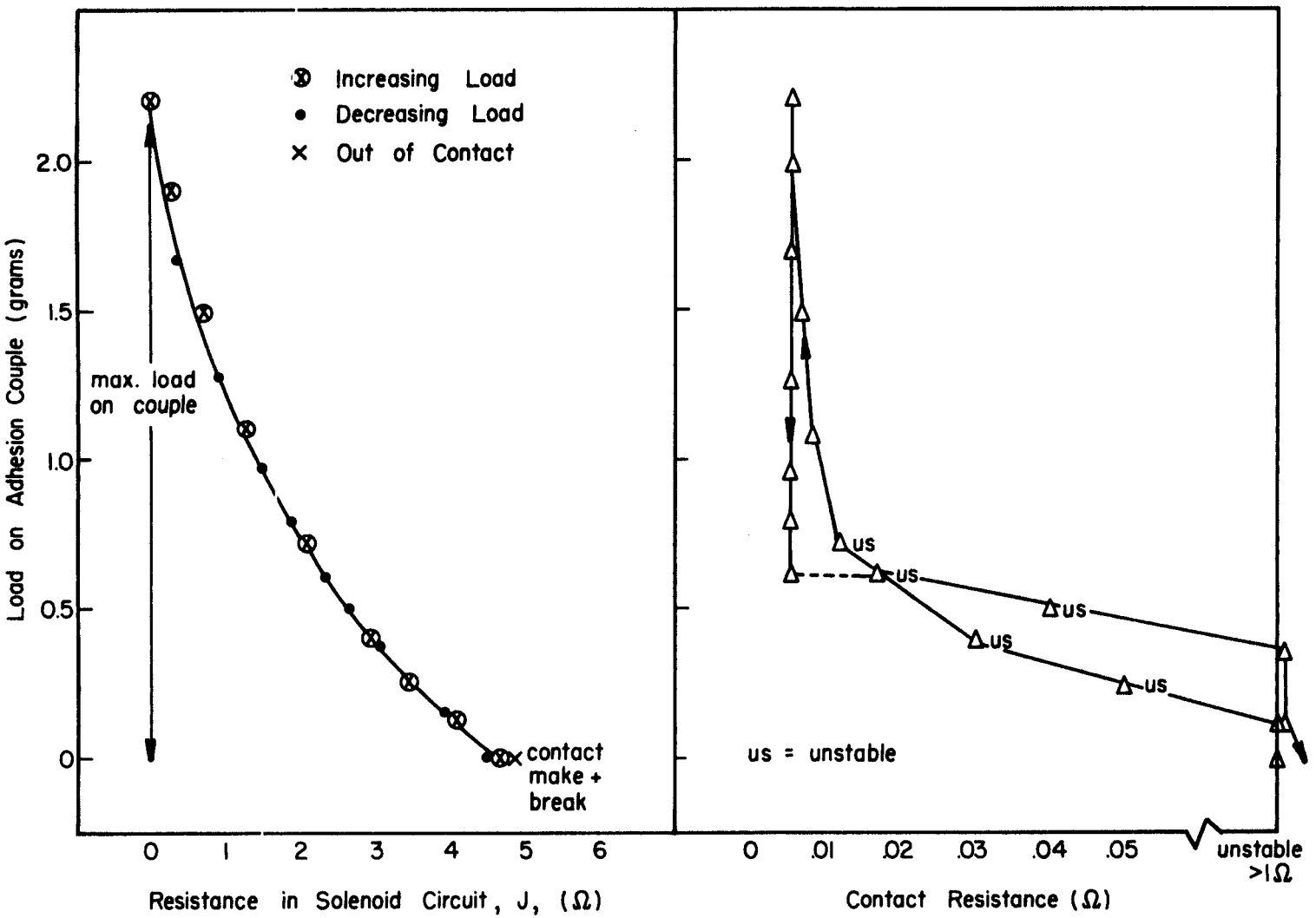

FIGURE 5 - Molybdenum-molybdenum adhesion cycle after extensive electron bombardment degas of samples (∿ 30 hrs. at > 1,000°C) and heating in oxygen and hydrogen atmospheres, pressure - 6 x 10^{-9} Torr.

after extensive surface cleaning techniques were employed, none of the systems presently studied show the spontaneous adhesion previously observed for the silver-silver, silver-nickel and nickel-copper (3) systems under very light loads. This present lack of adhesion may be due to an inherent property of the systems, or it may be that these harder materials are more difficult to clean than the softer ones previously studied. If it is due to an inherent property of the couple material, then one or both of the two factors governing adhesion mentioned above will be substantiated, namely,

1. that harder metal couples are more difficult to bond than softer couples because of a higher energy barrier due to the necessity of rearranging the more tightly held surface atoms,
2. the bonds formed between the harder metals under light loading are broken on the removal of the applied load by the relief of elastic stresses since these stresses are necessarily greater in magnitude than those caused by unloading the softer metals from comparable loads.

Whilst the former mechanism may be applicable, however, the titanium results show that the elastic relief forces are insufficient to rupture any bonds formed since significant adhesion was found after a couple loading of $\sim$ 1.5 grams, where the bulk interaction should be totally elastic, apart, of course, from the plastic deformation of surface asperities.

A further significance in the fact that the titanium couples showed adhesion when deformed solely elastically, is that this is at variance with previous reports (1) (2), that hexagonal metals are difficult to cold weld. These titanium results indicate, therefore, that the

atomic structure of metals is no criterion for adhesion.

It is felt, however, that the effects of contamination have not been totally eliminated from the present specimen surfaces. The reason for believing this, is best illustrated by Table I where the measured contact resistances of the couples studied are shown under various conditions. The previously reported Ag-Ag results are shown for comparison. The theoretical contact resistance is also shown for each couple and was derived by using the equation suggested by Holm (14):

$$R = \rho/2a \qquad (3)$$

where R is the contact resistance, ρ the specific resistivity of the metal and a the radius of the circular contact zone. This equation necessarily assumes one circular contact zone and the absence of contamination. Further, in the present case, the radius of the contact zone, a, was calculated assuming elastic interactions, by using Equation (1). Consequently, the theoretical contact resistance values shown are only approximations to what should be expected practically. Table I does, however, show that the observed contact resistance values obtained for titanium and tungsten are substantially above those predicted theoretically, and that the molybedenum values only approach the theoretical after prolonged specimen degas and surface cleaning procedures. The observed and theoretical contact resistance values for silver correspond as well as could be expected from the simple theory and, consequently, it must be concluded that the silver specimens are, as far as can be judged, contaminant free, whereas the tungsten, titanium and molybdenum surfaces are contaminated to some degree, even after rigorous surface cleaning procedures. The source of contamination is thought to be due to internal diffusion from the interior of the specimens to the surface subsequent to the employment of the cleaning techniques.

TABLE I

Metal couple	$\sim 10^{-6}$ Torr before bakeout	$\sim 10^{-9}$ Torr after bakeout	After 1st argon ion bombard.	After intermediate electron bombard. degas	After 2nd argon ion bombard.	Theoretical contact rest. at 1.5 gms load (ohms)
Ag-Ag[3]	.0037	.00250	.00087			.00197
W-W	$\sim$ .3	$\sim$ .3	.030	$\sim$ .07		.0124
Ti-Ti	unstable, > 1.0Å	unstable >1.0Å	.117	.0682	.0881	.00498
Mo-Mo	$\sim$ .3	$\sim$ .08	$\sim$.030	$\sim$ .019	$\sim$ .018*	.0128

Values are an average of 2-5 measurements, given in ohms, load range 1.3 - 1.7 grams.

* Values reduced to .011 ohms after prolonged degas electron bombardment, after heating in oxygen and hydrogen atmospheres.

Future Work

Although the present work shows a considerable reduction in the contact resistance of the Ti-Ti, W-W, and Mo-Mo couples after surface cleaning, together with indications of bonding in the Ti-Ti and Mo-Mo couples at heavier loads, it is felt that adhesion studies have not yet been done on clean metal couple surfaces. Consequently, further experiments have been planned for the above couples after the employment of even more rigorous surface cleaning and specimen degassing techniques than have been presently used.

Furthermore, the range of specimen loading will be increased by a factor of five,to ten grams in order to see what effect this has on the adhesion characteristics of the couples

REFERENCES

(1) Milner, D.R., and Rowe, G.W., Met. Rev., 28, Vol. 7, 433 (1962).

(2) Sikorski, M.E., Wear, 7, 144 (1964).

(3) Keller, D.V., Jr., Semi-Annual Report, Jan. 1966, for NASA, Grant NSG-483-1.

(4) Semenov, A.P., Wear, 4, 1 (1961).

(5) Erdmann-Jesnitzer, F., Aluminum, 33, 730 (1957).

(6) Bowden, F.P., and Rowe, G.W., Proc. Roy. Soc., 233A, 429 (1955).

(7) Keller, D.V., Jr., and Spalvins, T., Trans. Vac. Met. Conf., R.F. Bunshah, Ed. (1966), Amer. Vac. Soc. Pub. 149, Boston (1963).

(8) Williamson, J.B.P., Proc. Inst. Elec. Eng., 109A, No. 3, 224 (1962).

(9) Hertz, M., see Timoshenko, S., and Goodier, J.N., "Theory of Elasticity", McGraw-Hill Book Co., Inc., N.Y. (1951).

(10) Tabor, D., "The Hardness of Metals", Clarenden Press, Oxford, England (1951).

(11) Haas, T.W., and Jackson, A.G., J. Chem. Phys., 44, 8 (1966).

(12) Hagstrum, H.D., and D'Amico, C., J. Appl. Phys., 31, 4, 715 (1960).

(13) Davis, G.L., Nature, 181, 1198 (1958).

(14) Holm, R., "Electric Contacts Handbook", Springer-Verlag, Berlin, Germany (1958).